

Raney copper

This application claims priority to EP Application No. 00 103 546.8, filed on February 18, 2000, and U.S. Provisional Application No. 60/198,755, filed April 21, 2000, the
5 subject matter of each of which is hereby incorporated herein by reference.

BACKGROUND OF THE INVENTION

1. Field of the Invention

10 This invention relates to Raney copper, to a process for the production thereof and to a process for dehydrogenating alcohols.

2. Background Information

15 It is known to dehydrogenate diethanolamine to yield iminodiacetic acid (US 5,689,000; WO 96/01146; WO 92/06949; published patent application JP 091 55 195; US 5,292,936; US 5,367,112; CA 212 10 20).

SUMMARY OF THE INVENTION

20 The present invention provides Raney copper which is characterised in that it is doped with at least one metal from the group comprising iron and/or noble metal.

Doping may be achieved both by alloying the doping element with the Raney alloy, which consists of copper and
25 aluminium, and by impregnating the previously prepared Raney copper with the doping element.

The Raney copper according to the invention may contain the doping elements in a quantity of 10 ppm to 5 wt.%. Noble metal doping may amount to 10 to 50000 ppm, preferably 500
30 to 50000 ppm. The doping metals may be selected from the group comprising iron and palladium, platinum, gold, rhenium, silver, iridium, ruthenium and/or rhodium.

The Raney copper according to the invention may comprise meso- and macropores, but no micropores.

The initial formed alloy can contain more than 50% Cu so that the finished catalyst contains more residual Al than
5 normally found under the same activation conditions.

The initial formed alloy can be heat treated in air temperatures higher than 500 °C activation.

The initial formed alloy can contain more than 50% Cu and heat treated in air temperatures higher than 500 °C before
10 activation.

The average particle size of the Raney copper according to the invention may be $35 \pm 30 \mu\text{m}$.

The average particle size of the Raney copper according to the invention is of significance during use in oxidation
15 reactions or alcohol dehydrogenation reactions.

On repeated use, known Raney copper forms granules (agglomerates), so deactivating the Raney copper.

The Raney copper according to the invention doped with iron and/or noble metal is not deactivated by unwanted
20 granulation. Advantageously, the Raney copper according to the invention may readily be filtered.

The Raney copper according to the invention exhibits greater activity in the dehydrogenation of ethylene glycol than the Cr/Raney copper according to EP 0 620 209 A1 or
25 US 5,292,936.

The Raney copper according to the invention furthermore advantageously contains no toxic metals, such as chromium for example.

The present invention also provides a process for the
30 production of the Raney copper, which process is

characterised in that a copper/aluminium alloy is activated by means of an aqueous sodium hydroxide solution, the catalyst is washed, suspended in water, an iron salt or noble metal salt solution is added to this suspension, the
5 pH value of the solution is adjusted to a value from 4 to 11, the catalyst is separated from the solution and washed.

The present invention also provides a process for the production of the Raney copper, which process is characterised in that the doping metal is alloyed together
10 with copper and aluminium, is then activated by means of aqueous sodium hydroxide solution and the catalyst is washed.

The present invention also provides a process for the catalytic dehydrogenation of alcohols to their
15 corresponding carbonyls and carboxylic acids, which process is characterised in that a Raney copper doped with iron or noble metal is used as the catalyst.

The process according to the invention for the dehydrogenation of alcohols may be used for dehydrogenating
20 glycols and/or aminoalcohols. The catalyst may be used in the form of a suspension for such reactions.

The alcohols which may be dehydrogenated according to the invention may be mono- or polyhydric alcohols. Said
alcohols, including polyether glycols, may be aliphatic,
25 cyclic or aromatic compounds which react with a strong base to yield the carboxylate.

It is necessary in this connection that the alcohol and the resultant carboxylate are stable in a strongly basic
solution and that the alcohol is at least somewhat soluble
30 in water.

Suitable primary, monohydric alcohols may include:

aliphatic alcohols, which may be branched, linear, cyclic or aromatic alcohols, such as for example benzyl alcohol, wherein these alcohols may be substituted with various groups which are stable in bases.

- 5 Suitable aliphatic alcohols may be ethanol, propanol, butanol, pentanol or the like.

According to the invention, glycols may be oxidised or dehydrogenated to yield carboxylic acids. Glycols may, for example, be:

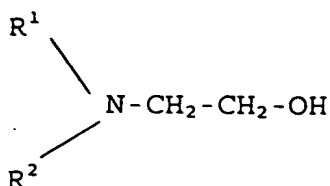
- 10 ethylene glycol
propylene glycol
1,3-propanediol
butylene glycol
1,4-butanediol

- 15 It is thus possible, for example, to dehydrogenate ethylene glycol to yield glycolic acid (monocarboxylic acid) and to produce the dicarboxylic acid oxalic acid by subsequent reaction with KOH.

- Aminoalcohols may also be dehydrogenated with the doped Raney copper according to the invention to yield the
20 corresponding aminocarboxylic acids. The amino alcohols may have 1 to 50 C atoms.

- It is accordingly possible, for example, to dehydrogenate N-methylethanolamine to yield sarcosine; THEEDA (tetrahydroxyethylethylenediamine) to yield the tetrasodium
25 salt of EDTA (ethylenediaminetetraacetate); monoethanolamine to yield glycine; diethanolamine to yield iminodiacetic acid; 3-amino-1-propanol to yield beta-alanine; 2-amino-1-butanol to yield 2-aminobutyric acid.

- 30 In one embodiment of the invention, the process according to the invention may be used to dehydrogenate aminoalcohols of the formula



in which R^1 and R^2 each mean hydrogen; hydroxyethyl; -
 5 $\text{CH}_2\text{CO}_2\text{H}$; an alkyl group having 1 to 18 C atoms; an
 aminoalkyl group having 1 to 3 C atoms; a
 hydroxyalkylaminoalkyl group having 2 to 3 C atoms and
 phosphonomethyl.

The aminoalcohols which may be used according to the
 10 invention are known. If R^1 and R^2 are hydrogen, the
 aminoalcohol is diethanolamine.

If R^1 and R^2 are hydroxyethyl, the aminoalcohol is
 triethanolamine. The resultant aminocarboxylic acid salts
 of these starting aminoalcohols should be the salts of
 15 glycine, iminodiacetic acid and nitrilotriacetic acid
 respectively. Further aminoalcohols comprise N-methyl-
 ethanolamine, N,N-dimethylethanolamine, N-ethylethanol-
 amine, N-isopropylethanolamine, N-butylethanolamine,
 N-nonylethanolamine, N-(2-aminoethyl)ethanolamine, N-(3-
 20 aminopropyl)ethanolamine, N,N-diethylethanolamine, N,N-
 dibutylethanolamine, N-methyldiethanolamine, N-ethyl-
 diethanolamine, N-isopropyldiethanolamine, N-butyl-
 diethanolamine, N-ethyl-N-(2-aminoethyl)-ethanolamine,
 N-methyl-N-(3-aminopropyl)ethanolamine, tetra(2-hydroxy-
 25 ethyl)ethylenediamine and the like.

Further examples of aminocarboxylic acid salts are the
 salts of N-methylglycine, N,N-dimethylglycine,
 N-ethylglycine, N-isopropylglycine, N-butylglycine,
 N-nonylglycine, N-(2-aminoethyl)glycine, N-(3-aminopropyl)-
 30 glycine, N,N-diethylglycine, N,N-dibutylglycine,
 N-methyliminodiacetic acid, N-ethyliminodiacetic acid,
 N-isopropyliminodiacetic acid, N-butyliminodiacetic acid,

N-ethyl-N-(2-aminoethyl)glycine, N-methyl-N-(3-amino-propyl)glycine, ethylenediaminetetraacetic acid etc..

R¹ or R² may also be a phosphonomethyl group, wherein the starting amino compound may be N-phosphonomethylethanol-amine and the resultant amino acid N-phosphonomethylglycine. If, of R¹ or R², one R = phosphonomethyl and the other R = -CH₂CH₂OH, the resultant amino acid would be N-phosphonomethyliminodiacetic acid, which may be converted in known manner into N-phosphonomethylglycine. If, of R¹ or R², one R = phosphonomethyl and the other R is an alkyl group, the resultant acid would be N-alkyl-N-phosphonomethylglycine, which may be converted into N-phosphonomethylglycine in accordance with US patent 5,068,404.

The process according to the invention may be performed at a temperature of 50 to 250 °C, preferably of 80 to 200 °C, and at a pressure of 0.1 to 200 bar, preferably at standard pressure to 50 bar.

The pressure is required because the alcohols have an elevated vapour pressure. If the pressure were too low, the alcohol would also be discharged when the hydrogen was discharged.

DETAILED DESCRIPTION OF THE INVENTION

Example 1: (Production of the catalyst according to the invention)

An alloy consisting of 50% Cu/50% Al is activated with an aqueous sodium hydroxide solution. The corresponding catalyst is washed until the sodium aluminate has been completely removed. Hexachloroplatinum is then added to the suspension of the washed catalyst. The pH value is adjusted and stirring of the suspension is continued. The doped catalyst is then washed. The platinum content of the catalyst is 1%. The activity of this catalyst for

dehydrogenating ethylene glycol is 299 ml of hydrogen per hour per gram of catalyst (c.f. Example 3).

Example 2: (Production of the catalyst according to the invention)

- 5 An alloy consisting of 50% Cu/50% Al is activated with an aqueous sodium hydroxide solution. The corresponding catalyst is washed until the sodium aluminate has been completely removed. Iron(III) chloride is then added to the suspension of the washed catalyst. The pH value is adjusted
10 and stirring of the suspension is continued. The doped catalyst is then washed. The iron content of the catalyst is 3%.

Example 3

- Dehydrogenation of ethylene glycol to yield sodium
15 glycolate and sodium oxalate by means of the activated catalyst according to the Example is performed at 108 °C and atmospheric pressure. 70 ml of ethylene glycol are first added to a heterogeneous suspension of 8 grams of catalyst and 70 ml of an aqueous sodium hydroxide solution.
20 The suspension is stirred at 400 rpm. The rate of reaction is measured by means of the quantity of hydrogen evolved between 30 and 90 minutes from the beginning of the reaction. The results are stated as ml of hydrogen per hour per gram of catalyst. The activity of this catalyst for
25 dehydrogenating ethylene glycol is 299 ml of hydrogen per hour per gram of catalyst.

Example 4 (Comparative Example)

- An alloy consisting of 50% Cu/50% Al is activated with an aqueous sodium hydroxide solution. The corresponding
30 catalyst is washed until the sodium aluminate has been completely removed. The activity of this catalyst for dehydrogenating ethylene glycol is 205 ml of hydrogen per hour per gram of catalyst.

Example 5 (Comparative Example)

A 50% Cu/50% Al alloy is activated with an aqueous sodium hydroxide solution. The corresponding catalyst is washed until the sodium aluminate has been completely removed.

5 Chromium nitrate is added to the suspension of the washed catalyst, the pH value adjusted, stirring of the suspension is continued and the doped catalyst washed once more. The chromium content in the catalyst is 2000 ppm. The activity of this catalyst for dehydrogenating ethylene glycol is
10 253 ml of hydrogen per hour per gram of catalyst.

Example 6 (Comparative Example)

A Cu/Al/V alloy is activated with an aqueous sodium hydroxide solution. The corresponding catalyst is washed until the sodium aluminate has been completely removed. The
15 content of V in the catalyst is 1%. The activity of the catalyst for dehydrogenating ethylene glycol is 253 ml of hydrogen per hour per gram of catalyst.

Example 7

Production of iminodiacetic acid with platinum on Raney
20 copper as catalyst.

The Example illustrates the conversion of diethanolamine (DEA) to yield the sodium salt of iminodiacetic acid (IDA) with Pt-doped Raney copper as catalyst.

The tests are performed in a 2 L Büchi autoclave. The
25 autoclave is equipped with a sparging agitator, which is operated at a standard speed of 500 min⁻¹(sic). The autoclave is equipped with a jacket. The temperature in the autoclave may be adjusted by means of a temperature controlled oil bath.

30 The following materials are initially introduced into the autoclave:

318.8 g of diethanolamine (3 mol)

508 g of aqueous NaOH solution (50 wt.%, 6.3 mol NaOH)

64 g of catalyst according to the invention: 1% Pt on Raney copper stored under water

5 370 g of H₂O, ultrasonically degassed

The autoclave is pressurised to 10 bar with nitrogen and adjusted to the reaction temperature (TR = 160°C). Once the reaction has begun, the evolved hydrogen is discharged, with the released quantity being determined by means of a
10 dry gas meter. The reaction is terminated after a period of 5 h and the autoclave cooled. The reaction products are flushed from the autoclave with degassed water, the catalyst filtered out and the dehydrogenation products analysed by ion chromatography.

15 As Table 1 shows, the catalyst used may be recycled repeatedly without appreciable loss of activity.

Table 1 Conversion of diethanolamine on Pt-doped Raney copper

Number of batches with catalyst	IDA yield [mol%]
1	94.3
2	92.5
3	98.6
4	96.8
5	95.0
6	94.7
7	90.9
8	91.8
9	93.4
10	95.8
11	97.7
12	93.5
13	95.7
14	92.6
15	90.0
16	n.d.
17	n.d.
18	95.2

[n.d. = not determined]

Example 6

- 5 Production of iminodiacetic acid with iron on Raney copper as catalyst.

The following materials are initially introduced into a 2 L autoclave:

318.8 g of diethanolamine (3 mol)

- 10 508 g of aqueous NaOH solution (50 wt.%, 6.3 mol NaOH)

64 g of catalyst according to the invention: 3% Fe on Raney copper stored under water

370 g of H₂O, ultrasonically degassed

The test is performed in a similar manner to Example 5. The yields listed in Table 2 are achieved; no deactivation of the catalyst is observable even after repeated use of the catalyst.

Table 2 Conversion of diethanolamine on Fe-doped Raney copper

Number of batches with catalyst	IDA yield [mol%]
1	95.3
2	99.1
3	99.0
4	n.d.
5	n.d.
6	91.9
7	n.d.
8	n.d.
9	n.d.
10	93.7
11	n.d.
12	n.d.
13	n.d.
14	94.0

10

Example 7

Comparative Example

Production of iminodiacetic acid on undoped Raney copper.

Pure Raney copper (Degussa catalyst BFX 3113W) is used under the conditions of Example 5. The Raney copper exhibits distinct deactivation after only a few batches. (Table 3)

15

Table 3 Conversion of diethanolamine on Raney copper

Number of batches with catalyst	IDA yield [mol%]
1	91.6
2	82.8
3	68.3
4	51.3

Example 8

Production of glycine with platinum on Raney copper as
5 catalyst.

The following materials are initially introduced into the 2
L autoclave:

307 g of monoethanolamine (5 mol)

420 g of aqueous NaOH solution (50 wt.%, 5.25 mol NaOH)

10 64 g of catalyst according to the invention: 1% Pt on
Raney copper stored under water

400 g of H₂O; ultrasonically degassed

The test is performed in a similar manner to Example 5. The
yields listed in Table 4 are achieved. No deactivation of
15 the catalyst is observable even after repeated use of the
catalyst.

Table 4 Conversion of monoethanolamine on Pt-doped Raney copper

Number of batches with catalyst	Glycine yield [mol%]
1	98.5
2	97.5
3	n.d.
4	n.d.
5	98.1

Example 9

- 5 Production of β -alanine with platinum on Raney copper as catalyst.

The following materials are initially introduced into the 2 L autoclave:

- 380 g of 3-amino-1-propanol (5 mol)
- 10 422 g of aqueous NaOH solution (50 wt.%, 5.25 mol NaOH)
- 64 g of catalyst according to the invention: 1% Pt on Raney copper stored under water
- 250 g of H₂O; ultrasonically degassed

The test is performed in a similar manner to Example 5.

- 15 The yields listed in Table 5 are achieved. No deactivation of the catalyst is observable even after repeated use of the catalyst.

Table 5 Conversion of 3-amino-1-propanol on Pt-doped Raney copper

Number of batches with catalyst	β -Alanine yield [mol%]
1	98.2
2	98.5
3	n.d.
4	n.d.
5	98.3

Example 10

- 5 Production of 2-aminobutyric acid with platinum on Raney copper as catalyst.

The following materials are initially introduced into the 2 L autoclave:

- 460 g of 2-amino-1-butanol (5 mol)
- 10 392 g of aqueous NaOH solution (50 wt.%, 5.25 mol NaOH)
- 64 g of catalyst according to the invention: 1% Pt on Raney copper stored under water
- 140 g of H₂O; ultrasonically degassed

The test is performed in a similar manner to Example 5.

- 15 The yields listed in Table 6 are achieved. No deactivation of the catalyst is observable even after repeated use of the catalyst.

Table 6 Conversion of 2-amino-1-butanol on Pt-doped Raney copper

Number of batches with catalyst	2-Amino-1-butyric acid yield [mol %]
1	99.2
2	98.1
3	n.d.
4	n.d.
5	98.9

BRIEF DESCRIPTION OF THE DRAWING

- 5 Figure 1 shows the advantage of the catalyst according to the invention illustrated by the example of the dehydrogenation or conversion of diethanolamine to yield iminodiacetic acid.

The catalyst according to the invention exhibits a
10 distinctly longer service life than the undoped Raney catalyst.